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ORGANOCLAY COMPOSITIONS PREPARED FROM ESTER QUATS AND
COMPOSITES BASED ON THE COMPOSITIONS

FIELD OF THE INVENTION

This invention relates generally to organophilic clays (hereinafter referred to as "organoclays"), and more specifically relates to organoclays prepared from smectite clays which have been treated with a quaternary ammonium compound of a type commonly referred to as an ester quat. Such ester quats are derived from 10 alkanolamine compounds whose hydroxyl groups are at least partially esterified with carboxylic acids to form a molecule with significant oleophilic properties. The resultant organoclays are useful as functional additives for organic based systems; where they may confer desired mechanical or physical properties sought for such systems.

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BACKGROUND OF THE INVENTION

Organoclays represent the reaction product of a smectite-type clay with a higher alkyl containing ammonium compound (often a quaternary), and have long 20 been known for use in gelling of organic liquids such as lubricating oils, linseed oil, toluene and the like and for use as rheological additives in a variety of organic based liquid systems and solvents. The general procedures and chemical reactions pursuant to which these organoclays are prepared are well known. Thus under appropriate 25 conditions the organic compound which contains a cation will react by ion exchange with clays which contain a negative layer lattice and exchangeable cations to form the organoclay products. If the organic cation contains at least one alkyl group containing at least ten carbon atoms then the resultant organoclays will have the property of swelling in certain organic liquids. Among the further prior art patents which discuss at length aspects of the preparation and properties of organoclays are U.S. Patents

Nos. 2,531,427; 2,966,506; 3,974,125; 3,537,994; and 4,081,496, all of which are incorporated herein by reference.

5 As utilized in the present specification, the term "smectite" or "smectite-type clays" refers to the general class of clay minerals with expanding crystal lattices, with the exception of vermiculite. This includes the dioctahedral smectites which include montmorillonite, beidellite, and nontronite, and the trioctahedral smectites, which include saponite, hectorite, and saucomite. Also encompassed are smectite-clays
10 prepared synthetically, e.g. by hydrothermal processes as disclosed in U.S. Patents Nos. 3,252,757; 3,586,468; 3,666,407; 3,671,190; 3,844,978; 3,844,979; 3,852,405; and 3,855,147, all of which are incorporated herein by reference.

15 In addition to their function as thixotropes, organoclays find numerous other applications. Of particular interest for present purposes are composite materials composed of an organic polymer and a smectite-type clay mineral, with the mineral being coupled to the polymer through ionic or other bonding. Prior art pertinent to such composites include U.S. Patent No. 2,531,3963, incorporated herein by reference, published November 28, 1950, wherein a reinforced elastomer is disclosed.
20 Smectite clays such as bentonite and hectorite are base exchanged with organic amines or salts thereof such as triethanolamine hydrochloride. Quaternary ammonium compounds can also be used. The resulting compounds, which are therefore "organoclays", are added to the lattices of elastomers. The organoclays can be added to the latex of any elastomer including natural rubber, and a large list of
25 polymers and/or copolymers is provided. The resulting compositions can be vulcanized.

Japan Laid Open Application S51(76)-109998, deriving from application SHO 50(1975)-3580 was published Sept 29, 1976, and is entitled "Method for
30 Manufacturing a Clay-Polyamide Composite". It discloses a method for

with a polymer compound. Among the polymers utilizable are polyamide resins, vinyl polymers, thermosetting resins, polyester resins, polyamide resins and the like. Related disclosures are found in U.S. Patents Nos. 4,739,007 and 4,889,885, both of which are incorporated herein by reference.

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In recent years the clay-polymer composite materials above discussed have been referred to as "nanocomposites", a term which reflects their property of exhibiting ultrafine phase dimensions, typically in the range 1-100nm. The number of nanocomposites based on smectite-type clays and linear thermoplastics is growing.

10 Wang and Pinnavaia, e.g., have reported delamination of an organically modified smectite in an epoxy resin by heating an onium ion exchanged form of montmorillonite with epoxy resin to temperatures of 200-300°C. Chemistry of Materials, vol. 6, pages 468-474 (April, 1994). Similarly in United States Patent No. 5,554,670, which is incorporated herein by reference, an epoxy-silicate
15 nanocomposite is disclosed which is prepared by dispersing an organically modified smectite-type clay in an epoxy resin together with diglycidyl ether of bisphenol-A (DGEBA), and curing in the presence of either nadic methyl anhydride (NMA), and/or benzylidimethyl amine (BDMA), and/or boron trifluoride monoethylamine (BTFA) at 100-200°C. Molecular dispersion of the layered silicate within the
20 crosslinked epoxy matrix is obtained, with smectite layer spacings of 100Å or more and good wetting of the silicate surface by the epoxy matrix. Additional recent references evidencing the increasing interest in nanocomposites incorporating organoclays in polymer matrices include United States Patent Nos. 5,164,440; 5,385,776; 5,552,469; and 5,578,672, all of which are incorporated herein by
25 reference.

Thus in a typical procedure for preparing a nanocomposite, the smectite clay, most commonly a montmorillonite, is treated with an organic ammonium ion to intercalate the organic molecule between the silicate layers of the clay, thereby substantially swelling or expanding the interlayer spacing of the smectite. (The
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BRIEF DESCRIPTION OF DRAWINGS

In the drawings appended hereto:

5 **FIGURE 1** is a wide angle X-ray scan pattern for an organoclay in accordance with the present invention;

FIGURE 2 is a wide angle X-ray scan pattern for a clay-polymer nanocomposite prepared using the organoclay depicted in Figure 1;

10 **FIGURE 3** is a wide angle X-ray scan pattern for a prior art ester quat-based organoclay;

FIGURE 4 is a wide angle X-ray scan pattern for a clay-polymer nanocomposite prepared using the organoclay the scan for which is depicted in Figure 2;

15 **FIGURE 5** is a wide angle X-ray scan pattern for a prior art quat-based organoclay, where the quat does not include esterified radicals; and

20 **FIGURE 6** is a wide angle X-ray scan pattern for a clay-polymer nanocomposite prepared using the organoclay the scan for which is depicted in Figure 5.

DETAILED DESCRIPTION OF THE INVENTION

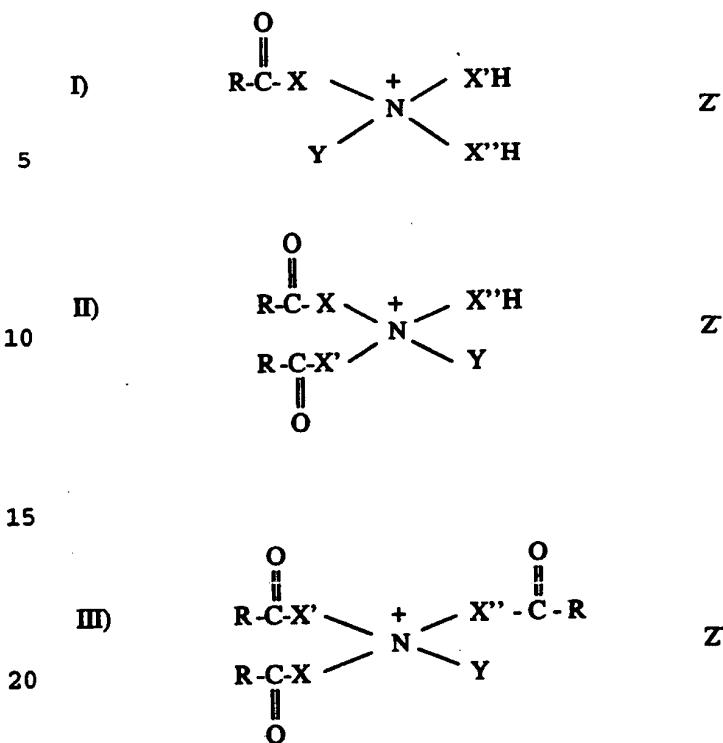
25 The quaternary ammonium compounds which are reacted with the smectite clays to produce the organoclays of the present invention are high in diester and low in triester content. They are obtained by reaction of C₁₂ - C₂₂ fatty acids or the hydrogenation products thereof, or a mixture of such acids, with an alkanolamine in the presence of an acid catalyst, wherein the ratio of fatty acid to alkanolamine is from about 1.40 to 2.0. The resultant ester amine reaction products are subsequently 30 quaternized to obtain quaternary ammonium salts for reaction with the smectite. In an

5 limited to, acid catalysts such as sulphonic acid, phosphorous acid, p-toluene sulphonic acid, methane sulphonic acid, oxalic acid, hypophosphorous acid or an acceptable Lewis acid in an amount of 500-3000 ppm based on the amount of fatty acid charge. In an embodiment, an acid catalyst is hypophosphorous acid. In an embodiment, 0.02 - 0.2 % by weight, and in other embodiments, 0.1 to 0.15 % by weight of acid catalyst, based on the weight of fatty acid, may be employed.

10 The esterification of fatty acids with alkanolamines is carried out at a temperature of from about 170° - 250°C until the reaction product has an acid value of below 5. After the esterification, the crude product is reacted with alkylating agents in order to obtain the quaternary ammonium product. Alkylating agents include C₁ - C₃ straight or branched chain alkyl halides, phosphates, carbonates, or sulfates, C₇ - C₁₀ aralkyl halides, phosphates or sulfates, and mixtures thereof. Examples of alkylating agents in an embodiment include, but are not limited to, methyl chloride, benzyl chloride, diethyl sulfate, dimethyl carbonate, trimethyl phosphate, dimethyl sulfate or mixtures thereof. Choosing the type and amount of alkylating agent employed is well within the skill of one in the art. In an embodiment, when dimethyl sulfate is the alkylating agent, 0.7 to 1.0 moles of dimethyl sulfate per mole of esteramine may be used. In other embodiments, 0.75 to 0.98 mol dimethyl sulfate per mole of esteramine 15 may be used in yielding the quaternized product.

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25 While such esterquats are typically prepared by reaction of the corresponding esteramine with dimethyl sulfate, applicants, in an embodiment, utilize an improvement to conventional quaternization processes. Dimethyl sulfate, a strong alkylating agent, is typically employed because of the excessively long reaction times encountered when weaker alkylating agents, such as methyl chloride, are employed. The quaternization reaction time can be significantly reduced, in many cases by 50% or more, if the esteramine mixture to be quaternized contains minimal amounts of



wherein:

X, X' and X'' are the same or different and are selected from straight or branched
 25 chain, optionally substituted oxyalkylene or polyoxyalkylene groups having from 2-6
 carbon atoms, in other embodiments, 3-6 carbon atoms, where the oxyalkylene units
 number from about 1-10, in other embodiments, 1-5, and in other embodiments, 1-2;
 each R group is individually selected from straight or branched chain, optionally
 substituted alkyl groups having from 11 to 23 carbon atoms, Y is an alkylphenyl
 30 group or a straight or branched chain optionally substituted C₁ to C₆ alkyl or alkylene
 group; and Z represents a softener compatible anion including, but not limited to,
 halogen, CH₃SO₄ or C₂H₅SO₄.

5 The reaction products may also include minor amounts of methyl trialkanolammonium salts and other impurities. The amount of diester in the final product (II) is generally greater than about 55% by weight and the amount of triester (III), based on the gas chromatograph of the ester amine, is generally less than about 25%, in other embodiments, less than 20% by weight based on the total amount of 10 quaternary ammonium salt product.

In an embodiment, product compositions contemplate an ester distribution within the following ranges: greater than about 55 wt% diester and less than about 25 10 wt% triester, with a total fatty acid IV of from about 20 to about 90; in other embodiments, greater than about 60 wt% diester and less than about 20 wt% triester, with a total IV of from about 30 to about 70; and in still other embodiments, greater than about 62 wt% diester and less than about 17 wt% triester, with a total IV of from 15 about 40 to about 60. In many instances triester content will be in the 10.0 to 17.0 wt% range. In an embodiment, the IV is between about 45 to about 58.

20 In an embodiment, the ratio of cis to trans double bonds of the above salts is in the range of from about 80:20 to about 95:5. In other embodiments, the cis:trans ratio is greater than about 90:10. In some embodiments, the amount of trans isomer is in 25 the range of from 5 to 9.5%.

There are several convenient methods for obtaining the desired cis:trans ratio of the quaternary ammonium salt product. One method is to produce the quaternary ammonium salt from cis-isomeric and trans-isomeric fatty acids after adjusting said 25 acids to the desired ratio.

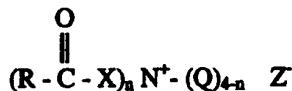
Another method is to produce the quaternary ammonium salt from the mixture after adjusting the ratio thereof by isomerizing a portion of the cis-isomeric fatty acid

or ester thereof into the trans-isomer, in the presence of a metallic catalyst. Other methods are readily apparent to and well within the skill of one of ordinary skill in the art.

5 The quaternary ammonium compounds may generally be prepared by reacting at least one C₁₂-C₂₂ fatty acid having a IV of from 20-90 with an alkanol amine in the presence of an acid catalyst. The ratio of acid to amine is, in one embodiment, in the range of 1.4 to 2.0, and the reaction is carried out at a temperature of from about 170°C to about 250°C until the reaction product has an acid value of below about 5.

10 A heat up rate of at least about 0.8°C per minute is employed in order to minimize triester formation. The esterification products are subsequently alkylated in order to obtain the quaternary ammonium product.

15 In another embodiment, the present invention contemplates a family of quaternary ammonium esters which are derived from ether alkanolamines. Said quaternary ammonium esters are of the general formula:



20 n is an integer of 1 or 2, R is a C₅ to C₂₃ straight or branched chain, optionally substituted alkyl group, each X can be the same or different and is selected from straight or branched chain, optionally substituted oxyalkylene or polyoxyalkylene groups having from 2-6 carbon atoms; each Q can be the same or different and is selected from a oxyalkylene or polyoxyalkylene group, or a straight or branched chain, optionally substituted alkyl, alkylene, alkylphenyl, hydroxyalkyl, hydroxyalkylene, wherein at least one of said Q groups is a C₂ to C₆ linear or branched chain oxyalkylene or polyoxyalkylene capped with a C₁ to C₆ alkyl, or an alkyl phenyl group; and Z is a compatible anion.

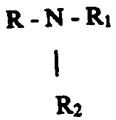
The above ester quat is generally prepared by reacting a fatty acid and/or fatty acid methyl ester as previously defined herein with an ether alkanolamine. The reaction is essentially the same as the reaction of said acid and/or said acid ester with an alkanolamine previously described herein, with an exception that the employment of a minimum heat up rate in order to achieve a high diester, low triester containing product is not performed. The reaction of fatty acid or fatty acid methyl ester with an ether alkanolamine may only produce mono- and di-substituted ester products. It is believed that the ether group is non-reactive and does not lead to the formation of a tri-substituted species. Accordingly, the heat up rate is less important when ether alkanolamines are employed as a reactant.

Further, employment of ether alkanolamines is beneficial in that they are more reactive with a broader range of alkylating agents, and the final products are easier to formulate and are more storage stable. Finally, the ratio of mono- and di-substituted species may be controlled by controlling the ratio of fatty acid/fatty acid methyl ester to ether alkanolamine.

In an embodiment, the preparation of a high diester quaternary ammonium mixture includes reacting:

- I) a C₁₁ - C₂₃ substituted or unsubstituted fatty acid or mixture of fatty acids having an Iodine Value of from about 20 to about 90, and having less than about 20% trans double bonds, with
- II) an ether alkanolamine of the formula:

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wherein R is a C₂ - C₆ alkyl ether, and each of R₁ and R₂ is independently selected from C₂ - C₆ hydroxyalkyl groups, wherein the molar ratio of said fatty acid to ether alkanol amine is from about 1.4 to about 2.0, in other embodiments, from about 1.6-1.9, and quaternizing the resultant ester amine mixture 5 in order to obtain an improved high diester quaternary ammonium mixture.

Ether alkanolamines include, but are not limited to, methoxyethyldiethanolamine, methoxypropyldiethanolamine, methoxybutyldiethanolamine and mixtures thereof. The high diester quaternary 10 ammonium mixture derived from ether alkanolamines in accordance with an embodiment generally has a diester content of at least 70 wt%, in other embodiments, greater than about 75 wt%, and in other embodiments, greater than about 80 wt% on a 100 wt% active basis.

15 Compositions having high diester content and low triester content demonstrate superior performance particularly in preparation of nanocomposites as compared to typical ester amine quaternary compounds.

In an embodiment, the smectite is a natural or synthetic clay mineral examples 20 of which include, but are not limited to, hectorite, montmorillonite, bentonite, beidelite, saponite, stevensite and mixtures thereof. In an embodiment, the smectite is hectorite.

In an embodiment, for preparing the organoclay composition, the smectite 25 mineral such as hectorite is crushed, ground, slurried in water and screened to remove grit and other impurities. In an embodiment, the smectite is converted to the sodium form if it is not already in this form. This may be effected, as known in the art, by a cation exchange reaction, or the clay may be converted via an aqueous reaction with a

soluble sodium compound. The smectite mineral is then subjected as a dilute (1 to 6% solids) aqueous slurry to high shearing in a suitable mill. In an embodiment, this shearing uses a homogenizing mill of the type wherein high speed fluid shear of the slurry is effected by passing the slurry at high velocities through a narrow gap, across which a high pressure differential is maintained. This type of action can e.g. be effected in the well-known Manton-Gaulin ("MG") mill, which device is sometimes referred to as the "Gaulin homogenizer". Reference may be made to U.S. patents Nos. 4,664,842 and 5,110,501, both of which are incorporated herein by reference, (assigned to the assignee Southern Clay Products Inc.) for further details of such mill.

5 The conditions for use of the MG mill may, in an embodiment, be substantially as in the said patents; e.g. the said pressure differential across the gap may be in the range of from 70,300 to 562,400 g/cm² with 140,600 to 351,550 g/cm² being more typical in representative operations.

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15 Depending upon the specifics of the equipment, pressures higher than 562,400 g/cm² may readily be used. The slurry to be treated may be passed one or more times through the MG mill. Among additional instrumentalities which may be effectively utilized to provide high shearing of the clay component, is the rotor and stator arrangement described in the assignee Southern Clay Products' U.S. Patent No.

20 5,160,454, which is incorporated herein by reference. Following the high shear step, the slurry is intermixed with the quaternary ammonium salt and the reaction slurry may again be subjected to high shearing by one or more passes through the MG or other mentioned instrumentalities. The slurry is thereupon dewatered, and the quaternary ammonium-treated clay dried and ground to provide a dry organoclay

25 product.

When used in composites such as nanocomposites, the organoclay compositions of the invention yield unexpected improvements in the mechanical and

other properties of the composite, including with respect to tensile strength, tensile modulus and flex modulus, all of which are highly significant attributes for the plastics and similar formulations.

5 The organoclays may be used in preparing nanocomposites by any of the methods which are set forth in the prior referenced patents, and with a large variety of polymerizable resins such as polyamides, epoxy, polyvinyl, polyacrylamide, etc.

10 The invention will now be illustrated by examples, which are to be regarded as illustrative and not delimitative of the invention. Unless otherwise indicated to the contrary, all parts and percentages are by weight.

Example 1

An organoclay composition was prepared from a smectite mineral clay which
15 was processed as above described, i.e. crushed, ground, slurried in water and screened, converted to its sodium form, and then subjected to high shear by being passed as a dilute slurry through an MG mill, and then as a slurry treated with the quaternary ammonium compound in accordance with the invention. This quaternary composition was a diester quat in admixture with further quaternary ammonium
20 compounds having esterified radicals, especially compounds having three esterified radicals (hereinafter "triester quats"); or compounds having a single esterified radical (hereinafter "monoester quats"). The reaction forming the organoclay was between the smectite clay and the quat mixture. The diester quat was present as greater than 55 wt% of the quaternary mixture; and the triester quat was present as less than 25
25 wt%, with the fatty acids corresponding to the esters in the mixture having a degree of unsaturation such that the iodine value ("IV") is from about 20 to about 90. A wide angle x-ray scan pattern for the product resulting from the reaction is shown in Figure 1, where the detected reflection intensity in counts/second is plotted against the D-

spacing in Angstrom Units. The 001 reflection peak indicates a remarkably high D_{001} spacing for the organoclay of 59.1 Å, and suggests that the organoclay will exhibit a very high exfoliation efficiency in nanocomposites.

5 Example 2

5 wt% of the organoclay powder of Example 1 was premixed with high impact polystyrene ("HIPS") pellets by mechanical means. 50 to 60 g of this dry blend was added to a Brabender mixer which was then operated at 60 rpm. The temperature of 10 the mixer was varied from 190° C to 230° C. The time of melt blending in the mixer was varied from 15 minutes to one hour. At the end of the prescribed time, the molten mixture was extruded from the Brabender. The resulting nanocomposite sample was prepared for x-ray analysis by pressing the mixture in a Wabash press with the platens heated to 150° C. at a pressure of 7,500 to 10,000 p.s.i. for one 15 minute. A 1-1/8" by 1-1/8" square was cut from the sample for analysis. The resulting wide angle x-ray scan pattern is shown in Figure 2. The D_{001} reflection peak of the organoclay is completely gone in this composite indicating very high exfoliation of the organoclay in the HIPS matrix.

20 Example 3

In this Example an organoclay sample was prepared using the procedure of Example 1, except that in this instance the quat used was a diester quat (based on tallow), which in part differs from the quat used in Examples 1 and 2 in including 25 methyl groups on the remaining two -N bonds, whereas the Example 1 quat includes a hydroxyethyl group on one of the said remaining -N bonds. A wide angle x-ray scan pattern for the product resulting from the reaction is shown in Figure 3. The 001 reflection peak indicates a D_{001} spacing for the organoclay of 39.5 Å, which is not as

high as the sample of Example 1, although still suggesting that the organoclay will exhibit a reasonably high exfoliation efficiency in nanocomposites.

Example 4

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The procedure of Example 2 was used in preparing a nanocomposite, with the organoclay being that prepared in Example 3. The wide angle x-ray scan of this nanocomposite is shown in Figure 4. The D_{001} reflection peak of the organoclay is completely gone in this composite indicating high exfoliation of the organoclay in the

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HIPS matrix. The peak in the curve marked as 34.2 is probably the 002 reflection. This would indicate an 001d spacing in the exfoliated clay of at least 70 Å.

Example 5

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In this Example an organoclay sample was prepared using the procedure of Example 1, except that the quat used was that disclosed for use in preparing the organoclays described in commonly assigned U.S. Patent No. 5,739,087, the contents of which is hereby incorporated by reference. The said quat is a branched chain structure, and is not an ester quat. The corresponding wide angle x-ray appears in Figure 5, from which it is seen that the 001 reflection peak indicates a D_{001} spacing for the organoclay of 19.0 Å, which is lower than the sample of Example 1, and neither as high as the spacing of the sample in Example 3. This indicates that the organoclay will exhibit a considerably lower exfoliation efficiency in

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25 nanocomposites.

Example 6

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